REMOVAL EFFICIENCY OF Zn(II) IONS FROM AQUEOUS EFFLUENTS ON DIFFERENT TYPES OF WASTE BIOMASS

EFICIENȚA ÎNDEPĂRTĂRII IONILOR DE Zn(II) DIN MEDII APOASE PRIN BIOSORBȚIE PE DIFERITE TIPURI DE DEŞEURI DE BIOMASĂ

NACU Gabriela[1]*, NEMEŞ Lăcrămioara[1], MOCANU Anca Mihaela[1], BULGARIU Laura[1]

*Corresponding author e-mail: gabriela_nacu2011@yahoo.com

Abstract. *In this study was analyzed the ability of three types of waste biomass for removal of Zn(II) from aqueous solution. The three types of biosorbents that have been used in experiments are: sawdust, mustard waste and soybean waste. These materials, which are waste from various branches of industry, can be used to remove metal ions from aqueous solutions, thus helping to reduce environmental pollution. The results for the influence of initial Zn(II) ions concentration and contact time on the removal efficiency from aqueous media were modelled using two isotherm models (Langmuir and Freunlich) and two kinetics models (pseudo-first order model and pseudo-second order model). The evaluation of biosorptive potential of these three types of waste biomasses in the removal processes of Zn(II) ions from aqueous solution was performed using the parameters obtained from the modelling.*

Key words: waste biomass, biosorption, aqueous solution, Zn(II) ions

Rezumat. *În acest studiu s-a analizat capacitatea a trei tipuri de deşeuri de biomasă de a îndepărta Zn (II) din soluții apoase. Cele trei tipuri de biosorbenți care au fost utilizate în experimente sunt: rumeguşul, deşeurile de muştar şi deşeurile de soia. Aceste materiale sunt deşeuri provenite din diverse ramuri ale industriei, şi pot fi utilizate pentru a elimina ionii metalici din soluții apoase, contribuind astfel la reducerea poluării mediului. Rezultatele privind influența concentrației inițiale a ionilor de Zn(II) şi a timpului de contact asupra eficienței îndepărtării acestuia din medii apoase au fost modelate utilizând două modele ale izotermelor de biosorbție (Langmuir şi Freudlich) şi două modele cinetice (modelul cinetic de ordin pseudo-unu şi modelul cinetic de ordin pseudo-doi). Evaluarea potențialului biosorptiv ale celor trei tipuri de deşeuri de biomase în procesele de îndepărtare a ionilor de Zn(II) din soluții apoase a fost realizată cu ajutorul parametrilor obținuți în urma modelării.*

Cuvinte cheie: deşeuri de biomasă, biosorbție, soluții apoase, ioni de Zn(II)

INTRODUCTION

With the development of economy, environmental pollution and large-scale ecological destruction have become increasingly serious, threatening the survival and development of all mankind (Dai *et al.*, 2018). The rapid urbanization and

[1] "Gheorghe Asachi" Technical University of Iaşi, Romania

rapid advance of industrialization has resulted in the excessive discharge of heavy metal-containing wastewater into the environment, seriously affecting human health (Zhang *et al.,* 2016).

Zn (II) is considered an essential element for growth and metabolism of living organisms (Das *et. al*, 2015) but consuming large amounts of zinc, even for a short period of time, can cause stomach cramps, feeling weak, dry throat, cough, generalized pain, chills, fever, nausea and/or vomiting. The various utilization of Zn(II) in industrial activities (such as electroplating, metal processing, deodorants and cosmetics industry, medicine and ointment industry, paint and pigments production and fertilizers manufacturing) leads to contamination of surface waters with this heavy metal (Ahmaruzzaman, 2011).

In recent years, various methods, such as biological treatment, flocculation, chemical precipitation, electrochemical techniques, membrane related processes, osmosis, adsorbtion, ion exchange, coagulation, etc. (Jawad *et al*., 2015, Rosales *et al*., 2017. Agwaramgbo *et al.,* 2013), are used for the treatment of industrial effluents containing metal ions before their discharge. But these methods are either expensive or inefficient for the removal when the metals are at high concentration or has other important disadvantages, such as poor selectivity, high costs, high energy consumption, generation of large amounts of waste sludge, etc. (Kanawade and Gaikwad, 2011; Fu and Wang, 2011), which requires certain precautions in their application on an industrial scale. The search for new technologies involving the removal of toxic metals from wastewaters has attracted attention to adsorption, who has been shown to be an effective and costeffective method for removing of heavy metals, including Zn(II) ions, from aqueous effluents (Ashrafi *et al.,*2015).

The biosorption potential of some waste biomasses for Zn(II) ions removal from aqueous solution was examined in this study in batch systems. For the experiments have been used three types of biomass: mustard waste biomass, soybean waste biomass and sawdust. These biosorbents are derived from biofuels production or wood industry. The experimental data obtained from the influence of initial Zn(II) ions concentration and contact time on the biosorption efficiency on each type of biomass were modelled using two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order). The parameters calculated for each model have allowed the evaluation of biosorption potential of these three types of waste biomasses in the removal processes of Zn(II) ions from aqueous solution.

MATERIAL AND METHOD

The experiments were conducted in batch system, using three types of waste biomasses as biosorbents: mustard waste biomass, soybeans waste biomass and sawdust. The sawdust comes from the coniferous wood processing industry, while mustard and soybean biomass wastes were prepared from mustard biomass and soybeans biomass after oil extraction in a Soxhlet extractor with n-hexane for 24 hour. Drying of all biosorbents was done in warm air, at 50-55 °C and after drying, they were mortared and stored in the desiccator.

The biosorption experiments were performed at room temperature (22 ± 0.5 °C), by mixing biosorbent samples (0.125 – 0.2 g) with 25 mL of Zn(II) ions solution of known concentration (5.23 – 209.24 mg/L), in 100 ml conical flasks. Working solutions of Zn(II) were freshly prepared by diluting the stock solution (containing 654 mg Zn(II)/L) with distilled water. The stock solution of Zn(II) was prepared by dissolving an appropriate amount of zinc nitrate in distilled water. The initial pH values of working solutions were obtained using 0.1 mol/L HNO_3 solution.

At the end of biosorption experiments, the phases were separated by filtration, and Zn(II) concentration in filtrate was spectrophotometrically analysed with xylenol orange (Digital Spectrophotometer S104D, λ = 570 nm, 1 cm glass cell, against distilled water), using a prepared calibration graph.

The biosorption capacity (q, mg/g) of each waste biomass for Zn(II) ions was calculated from experimental data, according with their definition. The mathematical equation of the isotherm models (Langmuir and Freundlich) and kinetics models (pseudo-first order and pseudo-second order) used for the modeling of the experimental data were taken from the literature (Gerente *et al.,* 2007).

RESULTS AND DISCUSSIONS

In our previous studies (Nacu *et al.,* 2017) we have shown that the optimal pH for Zn (II) retention on these biomass waste is around 6.00 and this value of pH was maintained in all experiments.

In figure 1 is illustrated the influence of initial Zn(II) ions concentration on the biosorption performances of the three types of biomass. As can be observed, the increase of Zn(II) ions concentration determined the increase of the biosorption performances of each waste biomass used as biosorbent; the highest adsorption capacity is assigned to soybean waste, followed by mustard and sawdust.

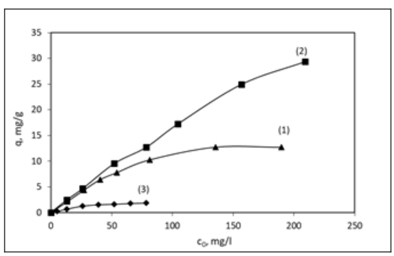
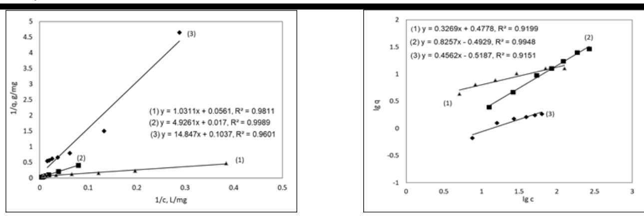


Fig. 1 Influence of initial Zn (II) ions concentration on the biosorption efficiency on (1) mustard waste biomass, (2) soybean waste biomass and (3) sawdust

This increased capacity of soybean biomass to retain Zn(II) ions can be explained by the presence of several functional groups on its surface in comparison to the other two types of waste studied.

The experimental data were analyzed using Langmuir and Freundlich isothermal models to obtain a quantitative measure of the Zn (II) retention capacity on biomass waste. The linear representations of each isothermal model are shown in figure 2, and the calculated isothermal parameters are shown in table 1.



(a) (b)

Fig. 2 Linear representations of Langmuir (a) and Freundlich (b) isotherm models for Zn(II) biosorption on (1) mustard waste biomass, (2) soybean waste biomass and (3) sawdust.

Table 1

Isotherm parameters for Zn(II) ions biosorption on the studied biosorbents

Isotherm model(*)		**Mustard waste biomass**	**Soybean waste biomass**	**Sawdust**
Langmuir	R^2	0.9811	0.9989	0.9601
	q_{max}, mg/g	17.8253	58.8235	9.6432
	K_L, g/L	0.0544	0.0034	0.0069
Freundlich	R^2	0.9189	0.9948	0.9151
	1/n	0.3269	0.8257	0.4562
	K_F, g/L	0.3328	3.1109	3.3014

It can be noticed that the (R^2) coefficient values are higher for the Langmuir model in comparison with the Freundlich model. Therefore, the Langmuir model has the higher applicability in the description of Zn(II) ions biosorption on the considered biosorbents. Consequently, we can assert that the biosorption process takes place up to the formation of monolayer coverage on the biosorbent surface (Gerente *et al.,* 2007). At the same time, by comparing the maximum biosorbtion capacities of the three biosorbents (q_{max}, mg/g), we can observe a higher biosorbtion potential of soybean waste in comparison to sawdust and mustard waste.

The contact time is the other parameter used to evaluate the biosorbtion efficiency of Zn(II) ions on the three types of waste biomasses and the experimental results, presented in figure 3, indicates that biosorbtion capacities increase with the contact time in all cases, reaching the maximum value after 30 minutes.

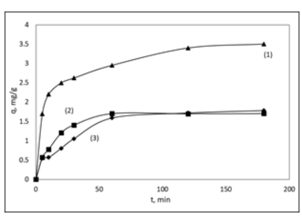
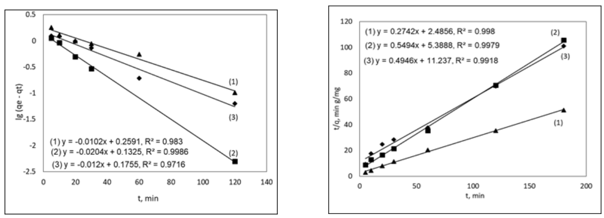


Fig. 3 Influence of contact time on the Zn(II) biosorption efficiency on (1) mustard waste biomass, (2) soybean waste biomass and (3) sawdust

For the kinetic modeling of the experimental data in figure 3, the pseudo-first kinetic model and the pseudo-second kinetic model were used and their linear representations was illustrated in figure 4. The values of the calculated kinetic parameters are shown in table 2.



(a) (b)

Fig. 4 Linear plots of pseudo-first order (a) and pseudo-second order (b) kinetics models, for Zn(II) biosorption on (1) mustard waste , (2) soybean waste and (3) sawdust

Table 2

Kinetics parameters for Zn(II) ions biosorption on the studied biosorbents

Kinetics model		**Mustard waste biomass**	**Soybean waste biomass**	**Sawdust**
Pseudo-first order kinetics model	R^2	0.983	0.9986	0.9716
	q_e, mg/g	1.8159	1.3567	1.4979
	k_1, 1/min	0.0102	0.0204	0.012
Pseudo-second order kinetics model	R^2	0.998	0.9979	0.9918
	q_e, mg/g	3.6469	1.8201	2.0218
	k_2, g/mg min	0.0302	0.056	0.0217

Accordingly with figure 4, the pseudo-second order kinetics model best describes Zn(II) ions biosorption on these three biosorbents and it can say that the biosorption process is limited by the chemical interactions between Zn(II) ions and functional groups present on the biosorbents surface.

CONCLUSIONS

1. To study the influence of the initial concentration of Zn (II) ions and contact time on aqueous effluent removal, three types of biomass waste were used (mustard, soybeans and sawdust) and the experiments were performed in the batch system.

2. The experimental results were modeled using two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order).

3. The obtained results have shown that soybean waste biomass has the higest biosorption potential for Zn (II) ions from aqueous solution, in comparison with sawdust and mustard waste biomass.

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REFERENCES

1. **Agwaramgbo L., Magee N., Nunez S.K., Mitt K., 2013 -** *Biosorption and chemical precipitation of lead using biomaterials, molecular sieves, and chlorides, carbonates, and sulfates of Na & Ca,* J. Environ. Protect. 4, 1251–1257.

2. **Ahmaruzzaman M., 2011 -** *Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals*, Adv. Colloid Interface Sci.166, 36–59.

3. **Ashrafi S.D., Kamani H., Arezomand H.S., Yousefi N., Mahvi A.H., 2015 -** *Optimization and modeling of process variables for adsorption of Basic Blue 41 on NaOH-modified rice husk using response surface methodology,* Desalin. Water Treat 57 (30), 14051-14059.

4. Dai Y., Sun Q., Wang W., Lu L., Liu M., Li J., Yang S, Sun Y., Zhang K, Xu J., Zheng W., Hu Z, Yang Y., Gao Y., Chen Y., Zhang X., Gao F., Zhang Y., 2018 - *Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review*. Chemosphere 211, 235-253

5. **Das D., Vimala R., Das N., 2015 -** *Removal of Ag(I) and Zn(II) ions from single and binary solution using sulfonated form of gum arabic-powdered mushroom composite hollow semispheres: Equilibrium, kinetic, thermodynamic and ex-situ studies*, Ecol. Eng. 75, 116–122.

6. Fu F., Wang Q., 2011 - *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management, 92, 407-418.

7. Gerente C., Lee V.K.C., Lee P., McKay G., 2007 - *Application of chitosan for the removal of metals from wastewaters by adsorption - mechanisms and models review*. Critical Reviews in Environmental Science and Technology, 37(1), 41–127.

8. **Jawad A.H., Rashid R.A., Mahmuod R.M.A., Ishak M.A.M., Kasim N.N., Ismail K., 2015 -** *Adsorption of methylene blue onto coconut (Cocos nucifera) leaf: optimization, isotherm and kinetic studies*. Desalin. Water Treat 57 (19), 8839-8853.

9. **Kanawade S.M. and Gaikwad R. W., 2011 -** *Removal of Zinc Ions from Industrial Effluent by Using Cork Powder as Adsorbent*, International Journal of Chemical Engineering and Applications, Vol. 2 , No. 3 , 199-201

10. **Nacu G, Nemeş (Negrilă) L., Bulgariu L, 2017 -** *Batch adsorption of Zn(II) ions from aqueous solution onto sawdust,* Rev. Roum. Chim. 62 (4-5), 439-447.

11. Rosales E., Meijide J., Pazos M., Sanrom_an M.A., 2017 - *Challenges and recent advances in biochar as low-cost biosorbent: from batch assays to continuous-flow systems*, Bioresour. Technol. 246, 176-192.

12. **Zhang J., Chen H., Chen Z., He J., Shi W., Liu D., Chi, H., Fuyi C., Wang W., 2016 -** *Microstructured macroporous adsorbent composed of polypyrrole modified natural corncob-core sponge for Cr (VI) removal*. RSC Adv. 64, 59292-59298.